

# Electronic structure of $\text{CeRu}_4\text{Sn}_6$ : a density functional plus dynamical mean field theory study

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The Kondo system  $\text{CeRu}_4\text{Sn}_6$  shows a strong anisotropy in its electric, optic and magnetic properties. We employ density functional theory plus dynamical mean field theory and show that the predominant Ce- $f$  state has total angular momentum  $J = 5/2$  and  $z$ -component  $m_J = \pm 1/2$  in agreement with recent X-ray absorption experiments. Even though  $\text{CeRu}_4\text{Sn}_6$  has the direct gap of a Kondo insulator through most of the Brillouin zone it remains weakly metallic. This is because of (i) a band crossing in the  $z$ -direction and (ii) a negative indirect gap.

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In  $f$ -electron systems such as  $\text{CeRu}_4\text{Sn}_6$  we have the generic situation that narrow, strongly interacting  $f$  bands hybridize with weakly correlated conduction bands, as exemplified by the periodic Anderson model. This gives rise to a hybridization gap at the crossing of  $f$  and conduction band, already without  $f$ - $f$  interaction e.g. in density functional theory (DFT). Electronic correlations strongly renormalize this gap, resulting in a gapped Kondo resonance which can be understood in a quasiparticle picture. If the gap is at the Fermi level one has a Kondo insulator; otherwise one has a metal with a typically heavy effective mass<sup>1,2</sup>. Even more complicated is the situation in anisotropic Kondo insulators such as  $\text{CeNiSn}$ <sup>3</sup>. Here, the physical properties such as the susceptibility and the conductivity are strongly anisotropic. One possible explanation is a hybridization gap with nodes<sup>4-6</sup> so that in some directions the bands cross the Fermi level whereas there is a gap in other parts of the Brillouin zone. Besides, also a V-shaped DOS<sup>7</sup> or extrinsic effects such as off stoichiometry, impurities<sup>8</sup> or topological surface states have been considered as a microscopic origin of the residual metallicity in some directions.

Such an anisotropy has also been observed in  $\text{CeRu}_4\text{Sn}_6$  single crystals<sup>9</sup> with a simpler, tetragonal  $I42m$  crystal structure<sup>10,11</sup> (Fig. 1): the optical conductivity shows a weak Drude-like feature in the  $a - a$  plane whereas it has a dip at low frequencies in the  $c$ -direction<sup>12</sup>. This has been confirmed by density functional theory plus dynamical mean field theory (DFT+DMFT)<sup>16,17</sup> calculations of the optical conductivity<sup>12</sup>. Likewise the thermopower<sup>13,18</sup>, resistivity<sup>19</sup> and magnetic properties<sup>15</sup> are strongly anisotropic.

In the present paper, we discuss the DFT+DMFT calculations in more detail. In particular we show that electronic correlations and the Kondo effect reverse the crystal field splitting between  $J = 5/2$   $|m_J| = 1/2$  and  $J = 5/2$   $|m_J| = 3/2$  Ce- $f$  states. Here,  $J$  is the total angular momentum and  $m_J$  its  $z$ -component. Consequently the  $|m_J| = 1/2$  states get predominantly occupied with decreasing temperature (increasing correlation effects).

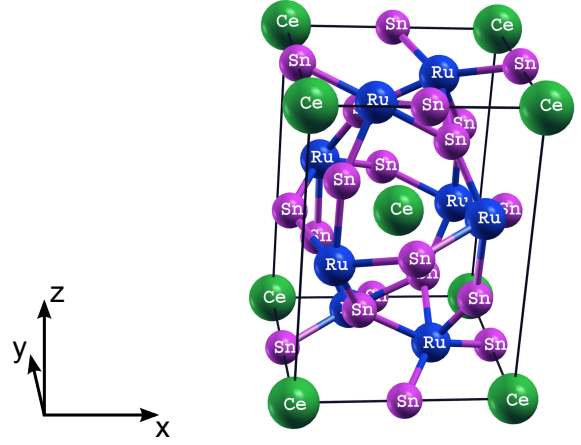


FIG. 1: Crystal structure of  $\text{CeRu}_4\text{Sn}_6$ .

Nonetheless, the evolving Kondo resonance at the Fermi level also contains  $|m_J| = 3/2$  states. This DFT+DMFT finding agrees with recent x-ray experiments<sup>14</sup> which best fit to  $|m_J| = 1/2$ . We also discuss why  $\text{CeRu}_4\text{Sn}_6$  remains metallic. In section I we present the DFT band-structure and Wannier orbitals. In Section II the orbitally resolved DMFT spectra and self energies and their temperature-dependence is discussed. Finally, Section III summarizes our results.

## I. DENSITY FUNCTIONAL THEORY

Starting point is the experimental tetragonal  $I42m$  structure of  $\text{CeRu}_4\text{Sn}_6$  with lattice parameters  $a = 6.8810$  Å, and  $c = 9.7520$  Å.<sup>20</sup> Here, the Ce atoms are surrounded by a "cage" with four nearest neighbor Ru atoms and four next nearest neighbor Sn atoms which are only 2% further away, see Fig. 1. Our first step is to calculate the DFT electronic structure with Wien2K<sup>21</sup> using the PBE-GGA potential and a fine  $k$ -mesh of 10000 points to obtain accurate results. Spin-orbit effects are important due to the heavy atoms and hence included.

The DFT partial densities of states for  $\text{CeRu}_4\text{Sn}_6$  are shown in Fig. 2. The calculation reveals a mixed manifold around the Fermi level with main contributions of Ce- $f$ , Ru- $d$  and Sn- $p$  character<sup>26</sup>. The narrow  $f$ -bands are essentially placed between 0.1 and 0.7 eV above the Fermi level in DFT. Because of the small hybridization tail below the Fermi level, the DFT  $f$ -filling is nonetheless surprisingly large, i.e., 0.7 electrons per Ce atom.

Fig. 2 (bottom) shows that the spin-orbit coupling separates the Ce- $f$  states into  $J = 5/2$  states, whose center of gravity is approximately around 0.2 eV, and  $J = 7/2$  states around 0.5 eV. The crystal field further splits the  $J = 5/2$  manifold into  $m_J = \pm 5/2$  character at higher energy and  $m_J = \pm 3/2$  as well as  $m_J = \pm 1/2$  states at essentially the same energy. The crystal field splitting between the latter is only  $\sim 0.05$  eV with  $m_J = \pm 3/2$  below  $m_J = \pm 1/2$ . This reflects in the small splitting in the  $f$ -level at  $\sim 0.2$  eV in Fig. 2 (bottom). Nonetheless, the largest contribution below the Fermi level has  $(J = 5/2, m_J = 1/2)$  character because these states hybridize more strongly with Ru- $d$  than the other  $f$  orbitals [the integrated weight below the Fermi level is larger for the  $m_J = \pm 1/2$  orbital in Fig. 2 (bottom)]. Apart from the  $f$  partial density of states, the major manifold in Fig. 2 is Ru- $d$  with traces of Sn- $p$ .

The corresponding bandstructure of  $\text{CeRu}_4\text{Sn}_6$  is shown in Fig. 3. There is a small dip above the Fermi level. This is due to a DFT direct gap between the highest lying occupied band (mainly Ru- $d$ ) and the lowest (unoccupied)  $f$  states with mixed  $m_J = \pm 3/2$  and  $m_J = \pm 1/2$  character. As one can see in Fig. 3, the valence and conduction band both touch the Fermi level however so that the indirect DFT band gap is zero. Also note that the lack of inversion symmetry around the Ce atoms lifts the degeneracy between the  $\pm m_J$  components.

Next, we do a projection onto maximally localized Wannier orbitals<sup>22</sup> using the Wien2Wannier<sup>23</sup> package. In this material, the spin-orbit coupling is crucial which makes the identification of adequate Wannier orbitals for modelling the low energy degrees of freedom more difficult. The decisive aspect is the choice of the atomic orbitals  $\phi_n^\uparrow$  and  $\phi_n^\downarrow$  for the Wien2Wannier localization to start with. For example, for  $(J = 5/2, m_J = +3/2)$  we start with

$$|\phi_{\frac{5}{2},+\frac{3}{2}}^\uparrow\rangle = -\sqrt{\frac{2}{7}}|\phi_{3,+1}^\uparrow\rangle + \sqrt{\frac{5}{7}}|\phi_{3,+2}^\downarrow\rangle \quad (1)$$

where  $|\phi_{3,+1}^\uparrow\rangle$  and  $|\phi_{3,+2}^\downarrow\rangle$  denote the  $|L = 3, m_L = +1, S = 1/2, m_s = +1/2\rangle$  and  $|L = 3, m_L = +2, S = -1/2, m_s = +1/2\rangle$  in the (lm)-basis, respectively; the prefactors are the Clebsch-Gordan coefficients. Besides the Ce- $f$  orbitals, we included all 40 Ru- $d$  and 36 Sn- $p$  orbitals in the Wannierization. Fig. 4 shows the most important Ce- $J = 5/2$  orbitals and their (fat-band) contribution to the bandstructure. The spread of the Ce- $f$  Wannier orbitals is:  $\Omega_{\frac{5}{2},\pm\frac{3}{2}} = 0.97 \text{ \AA}^2$ ,  $\Omega_{\frac{5}{2},\pm\frac{1}{2}} = 1.10 \text{ \AA}^2$ ,

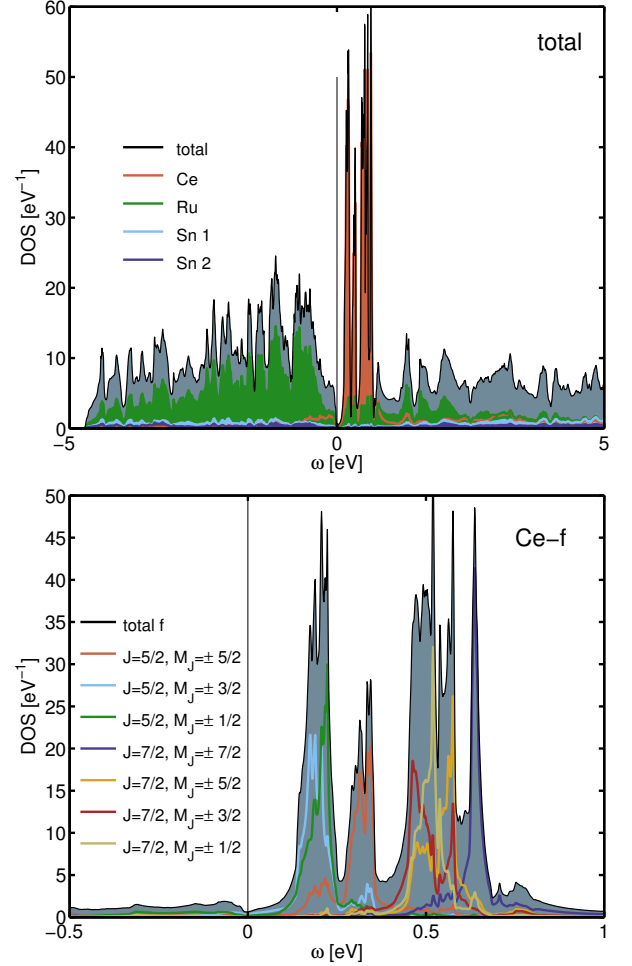


FIG. 2: Top: DFT partial density of states resolving the most important atom-wise contributions: Ce- $f$ , Ru- $d$  and Sn- $p$ . Bottom: Zoom in and further differentiation of the  $f$ -states in the  $(J, m_J)$ -basis.

$\Omega_{\frac{5}{2},\pm\frac{5}{2}} = 1.83 \text{ \AA}^2$ ,  $\Omega_{\frac{7}{2},\pm\frac{7}{2}} = 1.93 \text{ \AA}^2$ ,  $\Omega_{\frac{7}{2},\pm\frac{5}{2}} = 0.86 \text{ \AA}^2$ ,  $\Omega_{\frac{7}{2},\pm\frac{3}{2}} = 1.32 \text{ \AA}^2$ , and  $\Omega_{\frac{7}{2},\pm\frac{1}{2}} = 0.99 \text{ \AA}^2$ . That of the Ru- $d$  Wannier orbitals ranges from 2.32 to 5.79  $\text{\AA}^2$ , and that of the Sn- $p$  is even larger with  $\Omega$  from 5.89 to 18.14  $\text{\AA}^2$ .

## II. DFT+DMFT

We supplement the  $90 \times 90$  Wannier Hamiltonian by a local interaction  $U = U' = 5.5 \text{ eV}$  between all Ce- $J = 5/2$  states and subtract the double counting in the fully localized limit<sup>24</sup>. The corresponding Hamiltonian is then solved by DMFT with Hirsch-Fye quantum Monte Carlo<sup>25</sup> simulations. Note that the Ce- $J = 7/2$  orbitals remain unoccupied well above the Fermi level so that we do not need to include them as interacting in DMFT. For the sake of simplicity we neglect Hund's exchange which is justified since Ce only has about one  $f$ -electron and

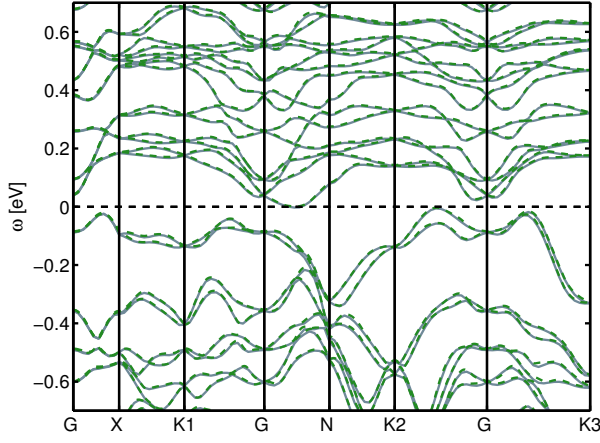


FIG. 3: DFT bandstructure around the Fermi level (solid,gray) perfectly reproduced by the Wannier orbital bands (dashed,green). Here and in the following figures,  $G = [0\ 0\ 0]$ ,  $X = [0\ 0\ \frac{1}{2}]$ ,  $K1 = [\frac{1}{2}\ 0\ \frac{1}{2}]$ ,  $N = [0\ \frac{1}{2}\ 0]$ ,  $K2 = [\frac{1}{2}\ \frac{1}{2}\ 0]$ ,  $K3 = [\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$ .

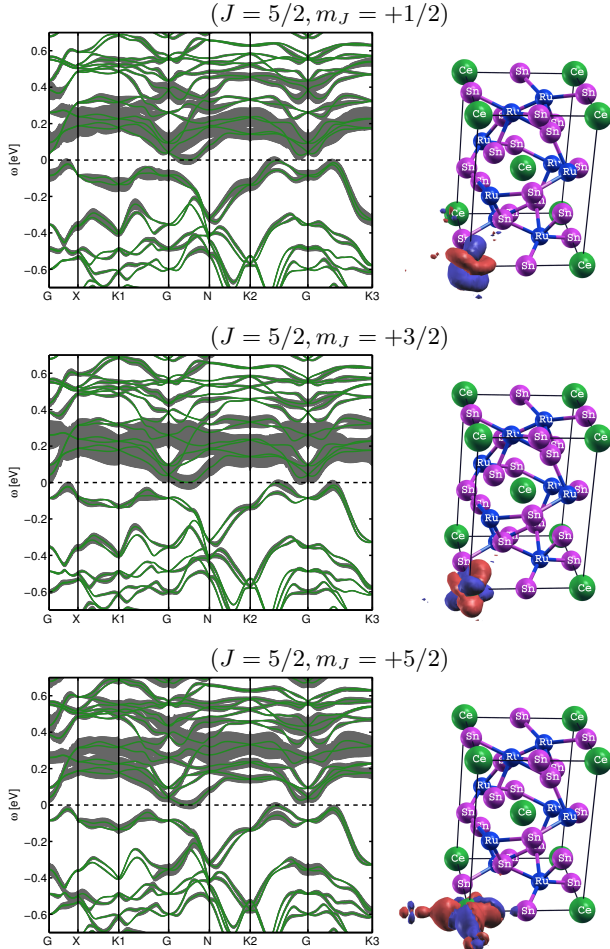


FIG. 4: Wannier orbitals for the Ce-f manifold in  $\text{CeRu}_4\text{Sn}_6$  and corresponding fat-band plots. For the charge density plots of the Wannier orbitals, the surface shows  $|w(r)|^2 = 5\ \text{Bohr}^{-3}$  and the color show the sign of the phase  $\phi$ , i.e. red (blue) for  $\cos(\phi(w(r)))$  positive (negative).

employ the same DMFT self energy for  $\pm m_J$ .

Let us start our discussion by looking at the orbitally-resolved local electronic densities. As already mentioned, in DFT the  $|m_J| = 1/2$  orbital is slightly more occupied. Specifically the electron density of the  $\text{Ce-}J = 5/2$  manifold is

$$\begin{aligned} n_{DFT} &= (n_{|m_J|=1/2}, n_{|m_J|=3/2}, n_{|m_J|=5/2}) \\ &= (0.34\quad 0.20\quad 0.28) \end{aligned} \quad (2)$$

Electronic correlations lead with decreasing temperature to higher  $|m_J| = 1/2$  occupations whereas the  $|m_J| = 5/2$  states get depopulated in DMFT:

$$n_{DMFT}(T = 1160\text{ K}) = (0.44\quad 0.38\quad 0.15), \quad (4)$$

$$n_{DMFT}(T = 290\text{ K}) = (0.60\quad 0.27\quad 0.08). \quad (5)$$

The higher  $|m_J| = 1/2$  occupation can be traced back to a reversal of the order of the crystal field levels. As discussed above, in DFT  $|m_J| = 3/2$  is the lowest crystal field state, 0.05 eV below  $|m_J| = 1/2$ . To this difference, we need now to add however the real part of the self energy, which altogether yields the so-called effective crystal field. The DMFT values (subtracting  $\mu$ ) for the three  $m_J$  states are, also see Fig. 5:

$$\Re\Sigma(T = 1160\text{ K}) - \mu = (-0.61\quad -0.26\quad 0.91)\text{ eV}, \quad (6)$$

$$\Re\Sigma(T = 290\text{ K}) - \mu = (-0.13\quad 0.13\quad 1.09)\text{ eV}. \quad (7)$$

That is the  $|m_J| = 1/2$  is shifted down and eventually becomes the lowest effective crystal field state in DFT+DMFT. We attribute this to the larger hybridization between  $|m_J| = 1/2$  and conduction electrons as well as to the Kondo effect (spin-flipping  $m_J = \pm 1/2$  to  $m_J = \mp 1/2$  is possible for conduction electrons with angular momentum 1/2).

The Kondo effect can be identified by the development of a Kondo resonance at the Fermi level when decreasing the temperature from  $T = 1160\text{ K}$  to  $290\text{ K}$ , see Fig. 6. Fig. 7 shows a zoom in and an orbital breakup. Clearly, the Kondo resonance at the Fermi level is made up from  $m_J = \mp 1/2$  and  $m_J = \mp 3/2$  states; the  $m_J = \mp 5/2$  states are at a somewhat higher energy due to the (correlation enhanced) crystal field splitting.

For  $\text{CeRu}_4\text{Sn}_6$ , there has been a long debate over the nature of the gap and its anisotropy. Fig. 8 shows the DFT+DMFT spectrum of the two most relevant orbitals,  $|m_J| = 1/2$  and  $|m_J| = 3/2$  of the  $\text{Ce-}J = 5/2$  manifold. There is a substantial broadening due to the imaginary part of the self energy which is still huge at  $290\text{ K}$ , indicating that we are still considerably above the Kondo temperature.

To get a better impression of the correlated bandstructure, we hence set the imaginary part of the self energy to (essentially zero) in Fig. 9. This way one can also mimic the low temperature behavior since the imaginary part of the self energy vanishes like  $\sim T^2$  around the Fermi

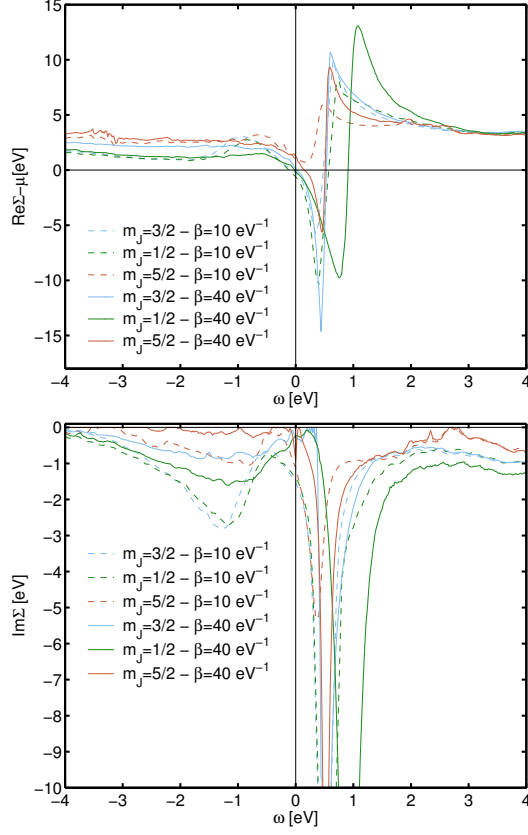


FIG. 5: Orbitaly resolved DMFT self energies for real frequencies  $\omega$  at inverse temperatures  $\beta = 10 \text{ eV}^{-1}$  and  $40 \text{ eV}^{-1}$ . Top: real part; bottom: imaginary part.

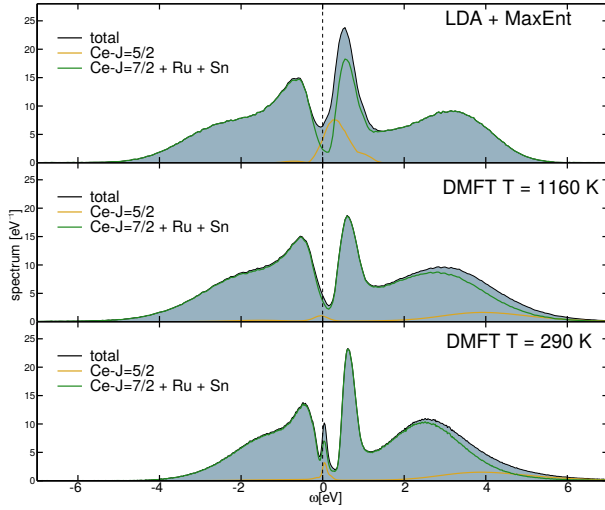


FIG. 6: DMFT spectra obtained by the maximum entropy method for  $T = 1160 \text{ K}$  (middle) and  $290 \text{ K}$  (bottom) compared to DFT (top).

level. One should keep in mind however, that the further build-up of the Kondo resonance might still reshuffle the bandstructure at lower temperatures.

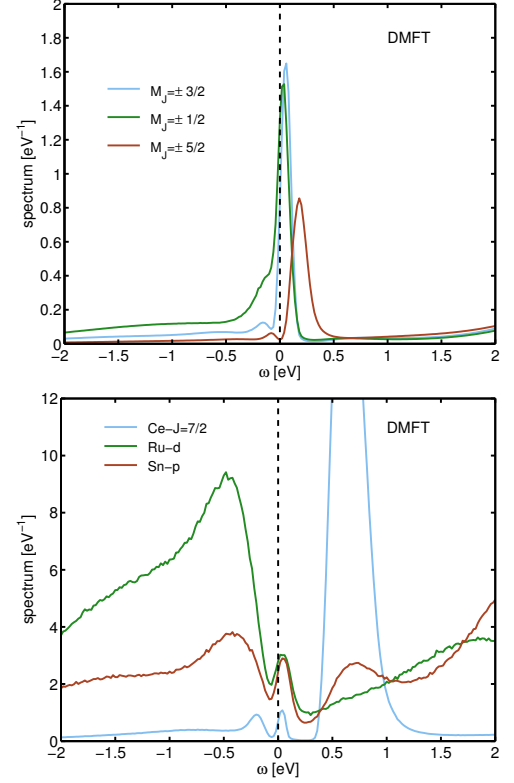


FIG. 7: DMFT spectra at  $T = 290 \text{ K}$  resolved for the  $J = 5/2$  orbitals (left) and corresponding contributions from the other manifolds (right).

Given the small crystal field splitting between  $|m_J| = 1/2$  and  $|m_J| = 3/2$  and its reversal by correlations as well as the much higher Kondo temperature for a  $SU(4)$  than a  $SU(2)$  Kondo effect, we can expect that both states will still contribute to the low temperature Kondo resonance.

In principle, Fig. 9 shows a Kondo insulator with a gap through most of the Brillouin zone. However, (i) along the  $z$  direction from  $G$  to  $X$  there a crossing of bands and hence no gap. Also in the other directions, there is (ii) a negative *indirect* band gap. These are two independent mechanisms of why  $\text{CeRu}_4\text{Sn}_6$  remains metallic with quite some anisotropy.

The origin of the gap is the usual Kondo insulator scenario, i.e., the hybridization between  $\text{Ce-}f$  and  $\text{Ru-}4d(\text{Sn-}5p)$  conduction bands. This can be seen by looking at the  $N$  and  $K_8$  point in Fig. 9 where there is a minimum of a (spin-split) conduction band around  $-0.2 \text{ eV}$  of mainly  $\text{Ru-}4d$  character. Around the Fermi level these band go over smoothly into a flat predominantly  $\text{Ce } |m_J| = 1/2$  band. In principle the same picture can also be found above the Fermi level. However, here it is somewhat less clear, since the conduction band maxima e.g. between  $K_8$  and  $G$  or  $K_3$  and  $G$  are not well separated from the other bands.

Around  $X$  and  $K_3$ , the whole low-energy bandstructure is shifted upwards. Here the gap is well above the



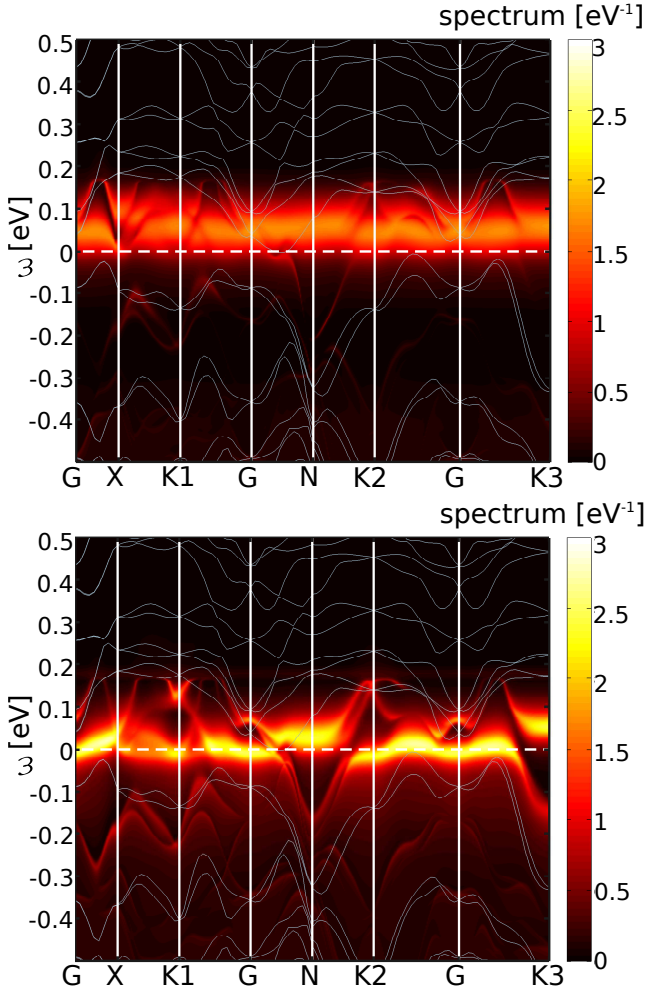


FIG. 8: DMFT  $k$ -resolved spectra of the two most important orbitals, the  $J = 5/2, m_J = 3/2$  (top) and  $J = 5/2, m_J = 1/2$  (bottom) orbital, at  $T=290$  K. White lines: DFT bandstructure for comparison.

Fermi level. Hence, we only have a direct band gap at most  $k$ -points whereas the indirect gap is zero, we have a Kondo semimetal. Note that the term semimetal has been used before, see e.g. Refs.<sup>27–29</sup>, to classify CeNiSn but to the best of our knowledge in another connotation, i.e., to denote the weak metallic behavior – even with the Ikeda-Miyake scenario<sup>4</sup> in mind, i.e., a hybridization gap with nodes and hence a crossing of conduction and  $f$  band.

Moreover, along the  $z$  direction, we even have a gapless crossing of bands, see Fig. 9. From Fig. 8 we infer that at  $G$  the lowest (spin-split) band is  $|m_J| = 1/2$ , the second one  $|m_J| = 3/2$  and the topmost the predominately Ru conduction band. Hence, this crossing is between  $|m_J| = 1/2$  and  $|m_J| = 3/2$ .

Altogether this scenario is much more complicated than a simple model with flat  $f$ -band. In Ref. 4 it was concluded that since  $|m_J| = 1/2$  orbitals have no nodes, the  $|m_J| = 1/2$  Kondo insulator has to be gapped

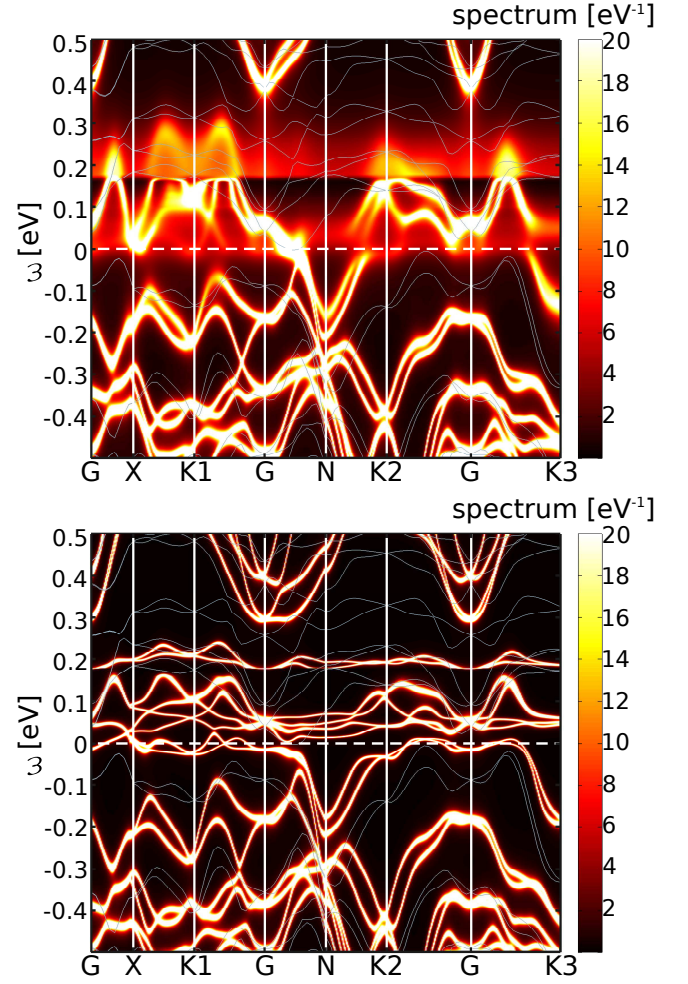


FIG. 9: DMFT  $k$ -resolved spectrum (top) and that for an artificial  $\Sigma(\omega) = \Re(\Sigma_{T=290K} \text{DMFT}(\omega)) + i0.005[\text{eV}]$  (bottom). White lines: DFT bandstructure for comparison.

throughout the Brillouin zone. This scenario is however too simple for CeRu<sub>4</sub>Sn<sub>6</sub>. First of all, there are both,  $|m_J| = 1/2$  and  $|m_J| = 3/2$ , bands in the vicinity of the Fermi level; and we (i) hence observe a crossing of bands. Even if we had no such crossing, we would (ii) nonetheless still have a Kondo semimetal with remnant metallicity instead of a Kondo insulator since the indirect band gap is negative. Because of these two reasons, the idealized modelling of Ref. 4 falls short of describing CeRu<sub>4</sub>Sn<sub>6</sub>.

### III. CONCLUSION

In perspective of new x-ray absorption experiments<sup>14</sup> we have presented further DFT+DMFT results for CeRu<sub>4</sub>Sn<sub>6</sub>. In agreement with experiment, the dominant Ce orbital is  $J = 5/2, |m_J| = 1/2$  which becomes the lowest crystal field level (and gets more occupied) when the Kondo effect sets in. However, there is also a secondary  $J = 5/2, |m_J| = 3/2$  contribution to the Kondo reso-

nance at the Fermi level. Because we have these two levels there is a band crossing along the  $z$  direction. Besides, the indirect Kondo gap is negative. That is even without band crossing we would still have a Kondo semimetal. Both mechanism on their own yield a remnant metallicity and anisotropy.

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